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KINETICS OF THE DISPLACEMENT REACTION BETWEEN FE AND CU<sub>2</sub>O AT TE--ETC(U)

MAY 79 G J YUREK, R A RAPP, J P HIRTH

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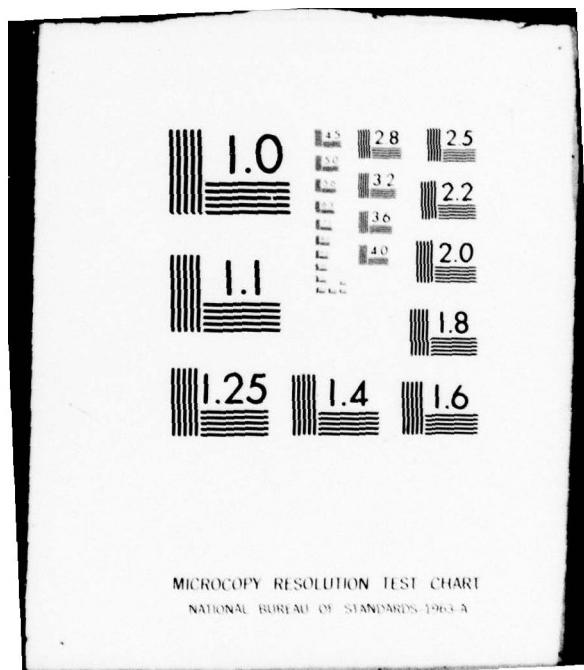
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AT TEMPERATURES BETWEEN 800 AND 1050°C

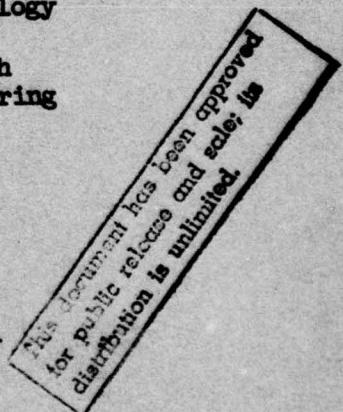
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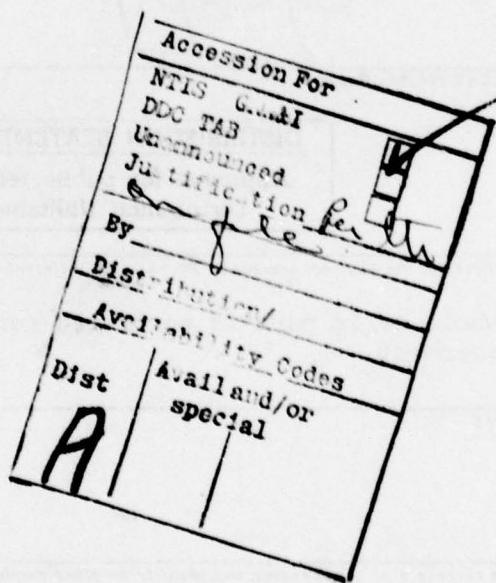
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KINETICS OF THE DISPLACEMENT REACTION BETWEEN Fe AND Cu<sub>2</sub>O  
AT TEMPERATURES BETWEEN 800 and 1050°C

by

Gregory J. Yurek\*, Robert A. Rapp\*\* and John P. Hirth\*\*

ABSTRACT

The products of the displacement reaction between solid iron and Cu<sub>2</sub>O in the temperature range of 800 to 1050°C are solid copper, wustite and magnetite. The product oxide in contact with the iron phase is in the form of rods embedded in a matrix of copper. A thin layer of copper separates the oxide rods from the Cu<sub>2</sub>O phase. The rates of growth of the product phases are controlled by solid-state counterdiffusion of oxygen and iron through the product phases, except for the initial stage of the reaction. A previously developed kinetic model for the diffusion-controlled growth of the product phases is employed to calculate the rates of growth of each of the product phases. Theoretical values of growth rates are in excellent agreement with experimental values for temperatures above 950°C. Below 950°C, the mechanism for the growth of the magnetite phase changes, which yields marked differences between the experimental and theoretical rates of growth. The mechanism for the displacement reaction below 950°C has not been determined.

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## 1. INTRODUCTION

A displacement reaction between solid iron and solid  $\text{Cu}_2\text{O}$  results in the formation of an aggregate of solid product phases between the reactant phases [1,2]. The product phases, which have been identified as wustite, magnetite and copper [3], are arranged in two zones between the reactant phases as shown schematically in Fig. 1. One zone is located adjacent to the iron and consists of rods of the product oxides in a matrix of copper. The other zone is a layer of copper that is located between the copper + oxide zone and the  $\text{Cu}_2\text{O}$ . This type of product arrangement has been classified as a lamellar-aggregate product morphology [2], although "rod-aggregate" product morphology is more descriptive.

Growth of the product phases of the  $\text{Fe}/\text{Cu}_2\text{O}$  displacement reaction requires solid-state diffusion of iron cations through the oxide rods and of oxygen atoms through the product copper layer. Electrons can migrate from the  $\text{Fe}/\text{FeO}$  interface to the tips of the oxide rods through the adjacent copper phase [see Fig. 1.]. The oxide rods grow at the boundary between the two product zones (the reaction front) as a result of the simultaneous arrival of iron cations, electrons and oxygen atoms. The copper layer grows at the  $\text{Cu}/\text{Cu}_2\text{O}$  interface where  $\text{Cu}_2\text{O}$  dissociates to yield metallic copper and oxygen dissolved in the copper.

Equations have been derived to calculate the equivalent fluxes of oxygen atoms and of iron cations at the reaction front [3]. The equivalent fluxes depend on two independent variables: (i)  $P_{\text{O}_2}^F$ , the

oxygen potential at the reaction front (see Fig. 1) and (ii)  $f$ , the volume fraction of oxide in the copper + oxide product zone. Two equations are necessary to solve for the two variables, and hence, for the equivalent fluxes at the front. One equation is obtained from a mass balance; i.e. the steady-state equivalent fluxes of iron and oxygen at the reaction front are equal. A second equation is obtained from the postulate [3] that the two variables adjust such that the maximum equivalent fluxes steady state, thereby maximizing the reaction kinetics. An analytical solution for the two variables has not been found; however, values for the equivalent fluxes can be computed as a function of  $f$  or  $P_{O_2}^F$  after one of the variables is eliminated from the flux equations. Theoretical values of  $f$  and  $P_{O_2}^F$  can then be used to calculate the rates of growth of the various product phases. Predicted reaction rates for the  $Fe/Cu_2O$  displacement reaction at 1000°C were found previously to be in good agreement with experimental reaction rates [3]. The purpose of the present paper is to extend the experimental and calculated results for the  $Fe/Cu_2O$  displacement reaction to temperatures between 800 and 1050°C.

## 2. THEORETICAL ANALYSIS

The equations and data that are necessary to calculate the equivalent fluxes of iron cations and oxygen atoms at the reaction front (Eqs. (34) and (35) of [3]) are presented in this section with some modifications.

## 2.1 Phases Present

The upper limit of temperature for applicability of the kinetic model for the Fe/Cu<sub>2</sub>O reaction is 1065°C, which is the eutectic temperature between copper and Cu<sub>2</sub>O. The formation of oxides in addition to wustite in the product zone depends on the kinetically established value of P<sub>O<sub>2</sub></sub><sup>F</sup> at the temperature of interest. The oxygen potential in the product zone varies from that for equilibrium between iron and wustite to that for equilibrium between copper and Cu<sub>2</sub>O. According to the oxygen potentials for equilibria among the compounds in the Cu-Fe-O system [4,5,23], wustite, magnetite and delafossite (CuFeO<sub>2</sub>) are possible product oxide phases in the temperature range of 800 to 1050°C. The oxygen partial pressure for equilibrium between copper, magnetite and delafossite is sufficiently close to the partial pressure for equilibrium between copper and cuprous oxide that delafossite is not a likely product phase; i.e. as P<sub>O<sub>2</sub></sub><sup>F</sup> approaches P<sub>O<sub>2</sub></sub> (Cu/Cu<sub>2</sub>O), the diffusion-controlled growth of the product copper layer must approach zero. Because delafossite was not observed experimentally it is not considered further in the analysis.

## 2.2 Parabolic Rate Constants for Oxides

Calculation of the equivalent fluxes of iron cations and oxygen atoms at the reaction front requires an evaluation of the parabolic rate constants for the diffusion-controlled growth of

wustite,  $k_p(Fe_vO)$ , and of magnetite,  $k_p(Fe_\delta O)$ . The Fe/O ratios for these oxides,  $v$  and  $\delta$ , are taken as average values of the Fe/O ratios over their ranges of stability. The Fe/O ratio for magnetite is approximately 0.75 for the entire temperature range of interest. The Fe/O ratio for wustite exhibits a considerable variation with oxygen potential at each temperature in the range of 800 - 1050°C. The average values of  $v$  given in Table I were calculated from the data for wustite compiled by Giddings and Gordon [5]. The use of an average Fe/O ratio for wustite is justified on the basis of a recent paper [6].

The parabolic rate constant for the diffusion-limited growth of an oxide  $Me_aO$  on a metal Me in an oxygen-containing gas is given by

$$k_p(Me_aO) = \frac{1}{2a^2} \int_{P'_{O_2}}^{P''_{O_2}} (D_{Me}^T / g_{Me}) d \ln P_{O_2}$$

where  $D_{Me}^T$  is the tracer diffusion coefficient for Me cations in  $Me_aO$ ,  $g_{Me}$  is the correlation factor for cation diffusion in  $Me_aO$  and  $P'_{O_2}$  and  $P''_{O_2}$  are the oxygen partial pressures at the metal/oxide and oxide gas interfaces, respectively. Equation (1) is a slightly modified form [7] of the equation derived by Wagner [8,9] for the parabolic rate constant. The major assumptions involved in the derivation of Eq. (1) are that (i) the variation in stoichiometry for  $Me_aO$  is small, (ii)  $Me_aO$  is an electronic conductor and (iii) the mobility of the cations is much greater than the mobility of anions in  $Me_aO$ .

These assumptions apply for magnetite with  $\alpha = 0.75$ .

Assumptions (ii) and (iii) apply for  $\text{Fe}_\nu\text{O}$ . Assumption (i) is not strictly applicable for  $\text{Fe}_\nu\text{O}$ , but the use of the average values  $\bar{v}$  at the temperatures of interest is justified on the basis of the results in ref. [6].

When both wustite and magnetite are present in an oxide growing under diffusion control, not all of the cations that enter the wustite phase at the  $\text{Fe}/\text{FeO}$  boundary contribute to the growth of the wustite phase at the  $\text{FeO}/\text{Fe}_3\text{O}_4$  phase boundary; some of the cations must diffuse further through the magnetite phase to contribute to the growth of the magnetite at the reaction front [3]. When this partitioning of cations between the two phases is included in the analysis, the following relationship is obtained between  $k_p(\text{Fe}_\delta\text{O})$ , the parabolic rate constant calculated with the aid of Eq. (1), and  $k'_p(\text{Fe}_\delta\text{O})$ , the rate constant for growth of magnetite in contact with a growing wustite phase [3,10]:

$$k'_p(\text{Fe}_\delta\text{O}) = [1 + \xi v_{\text{Fe}_\delta\text{O}} / n v_{\text{Fe}_\nu\text{O}}]^{-1} k_p(\text{Fe}_\delta\text{O}) \quad (2)$$

where  $\xi$  and  $n$  are, respectively, the thicknesses of the growing layers of  $\text{Fe}_\nu\text{O}$  and  $\text{Fe}_\delta\text{O}$ .

The equivalent form for  $\text{Fe}_\nu\text{O}$  is given by [3,10]

$$k'_p(\text{Fe}_\nu\text{O}) = [1 + \delta n v_{\text{Me}_\nu\text{O}} / v \xi v_{\text{Me}_\delta\text{O}}]^{-1} k_p(\text{Fe}_\nu\text{O}) \quad (3)$$

and the parabolic rate constant for the total oxide layer is given by

$$k_p(\text{oxide}) = \{[k'_p(\text{Fe}_v\text{O})]^{1/2} + [k'_p(\text{Fe}_\delta\text{O})]^{1/2}\}^2 \quad [4]$$

### 2.3 Transport Properties of the Oxides

The transport properties of wustite and magnetite that are necessary to solve Eq. (1) have been redetermined subsequent to publication of ref. 3. The tracer diffusion coefficients and the correlation factors for diffusion of iron cations in wustite were measured by Chen and Peterson [11] at approximately 800, 1000 and 1200°C. Data at each temperature of interest in the range of 800 to 1050°C were obtained [12] by interpolating the data of Chen and Peterson with the aid of composition data compiled by Giddings and Gordon [5]. The values obtained for the quotient  $D_{\text{Fe}}^T/g_{\text{Fe}}$ , which is the self-diffusion coefficient for cations in wustite, are listed in Table I.

The tracer diffusion coefficients for iron cations in magnetite have been measured as a function of oxygen partial pressure in the temperature range of 900 to 1400°C by Dieckmann and Schmalzried [13-15]; their results were extrapolated to 800 and 850°C. Magnetite contains excess iron at low oxygen potentials, but it is deficient in iron at high oxygen potentials [13-15]. Diffusion by a vacancy mechanism predominates at high oxygen potentials. The correlation factor for diffusion by a vacancy mechanism in magnetite

is  $g_{Fe} = 0.781$  [15]. Diffusion may take place by an interstitial mechanism or by an intersticialcy mechanism in magnetite at low oxygen potentials [14]. While the exact mechanism has not yet been determined, inspection of the spinel structure of magnetite suggests that an intersticialcy mechanism would be energetically favorable relative to an interstitial mechanism because the latter would involve very close spacings of cations.

If the interstitial cations in iron-excess magnetite diffuse by an intersticialcy mechanism, then the correlation factor for cation transport could be less than unity. An intersticialcy mechanism could conceivably involve all combinations of normally filled and empty tetrahedral and octahedral sites. One simple possibility, however, is an intersticialcy mechanism that involves only normally filled and empty octahedral sites. Each cation on a normal octahedral site is surrounded by six normally empty nearest-neighbor interstitial sites that are octahedrally coordinated. A tracer cation on any one of the six interstitial sites can displace the cation on the normal site to any one of the five empty interstitial sites. Inspection of the structure suggests, however, that the displacement would be collinear. If a collinear intersticialcy mechanism is operative, the angle between the jump vectors of the tracer cation and the cation on the normal site is zero. On its next jump, then, the tracer has a greater than random probability of jumping back to its original interstitial

site, and the motion of the tracer cation is correlated.

The correlation factor for a collinear interstitialcy mechanism for octahedrally coordinated normal and interstitial cations in magnetite has not been calculated. Compaan and Haven [16], however, have used an electrical analog technique to determine correlation factors for a number of similar interstitialcy mechanisms. For collinear interstitialcy diffusion of cadmium cations in  $\text{CdCl}_2$  (rhombohedral structure), where octahedrally coordinated interstitial cation sites have nearest neighbor cation sites in octahedral coordination as in magnetite, both the x- and z-components of the correlation factor are equal to 0.4. Chen and Peterson [11] interpret their measurements of correlation factors in oxygen-rich wustite in terms of a model of Roth [17] and Koch and Cohen [18] in which clusters of vacancies on octahedral cation sites group about occupied tetrahedral sites in a configuration resembling the structure of magnetite. For oxygen-rich wustite at  $807 < T < 1200^\circ\text{C}$  the measured  $g_{\text{Fe}}^{\Delta K} \approx 0.3$ , where  $\Delta K$  is the fraction of the total translational kinetic energy at the saddle point for a diffusion jump [11]. A value of 0.58 for  $\Delta K$  yields  $g_{\text{Fe}} = 0.78$  for wustite in equilibrium with iron. If  $\Delta K$  is assumed to be independent of composition, then  $g_{\text{Fe}}$  varies between 0.5 and 0.59 for wustite in equilibrium with magnetite in the range of 800 to  $1050^\circ\text{C}$ . Thus, a low value for the correlation factor in iron-rich magnetite seems likely.

On the basis of the above discussion, we assume that the correlation factor for cation diffusion in magnetite at low oxygen pressures is 0.4. Thus, the expression for  $D_{\text{Fe}}^T/g_{\text{Fe}}$  in

Eq. (1) becomes

$$\frac{D_{Fe}^T}{g_{Fe}} = \frac{D_I}{0.4} P_{O_2}^{-2/3} + \frac{D_V}{0.781} P_{O_2}^{2/3} \quad (5)$$

where the coefficients  $D_I$  and  $D_V$  from Dieckmann and Schmalzried [15] are the interstitial and vacancy components of diffusion in magnetite, respectively. Because  $g_{Fe}$  is less certain than the other parameters in the analysis, however, data are also analyzed for comparison in terms of Eq. (5) with the factor 0.4 replaced by unity.

#### 2.4 Molar Volumes of Oxides

An average molar volume of magnetite was calculated using a density of  $5.18 \times 10^{-6} \text{ g/m}^3$  for  $Fe_3O_4$ . An average molar volume of wustite at each temperature was estimated from the data of Hayakawa et al. [19] for the variation of the lattice parameter of wustite with composition at 950 and 1050°C. The average molar volume of wustite was assumed to vary linearly with temperature. The average values are listed in Table I.

#### 2.5 Transport Properties of Copper

The flux of oxygen through the product copper layer is proportional to the solubility-diffusivity product,  $N_O^{Cu} D_O^{Cu}$ , where  $N_O^{Cu}$  is the atom fraction of oxygen dissolved in copper and  $D_O^{Cu}$  is the diffusion coefficient for oxygen in copper. According to

Ramanarayanan and Worrell [20], the solubility-diffusivity product for the temperature range of 800-1000°C is given by

$$N_O^{Cu} D_O^{Cu} = (8.8_{-4.9}^{+11.1} \times 10^{-2}) v_{Cu} \exp\left(\frac{-200,832 \pm 8368J}{RT}\right) \quad (6)$$

where  $v_{Cu}$ , the molar volume of copper, is equal to  $7.13 \times 10^{-6} \text{ g/m}^3$ . The solubility-diffusivity product determined by Pastorek and Rapp [21] is a factor of approximately two higher than that calculated from Eq. (6). Values of  $N_O^{Cu} D_O^{Cu}$  measured by Wood, et al. [22] and by Rao and Tare [23] are slightly lower than those calculated from Eq. (6). A recent determination of the maximum solubility of oxygen in copper for temperatures in the range of 806 to 1050°C by Horrigan [24] yielded values that are 70-80% lower than those measured by Pastorek and Rapp [21]. Thus, the solubility-diffusivity product of Eq. (6) determined by Ramanarayanan and Worrell [20] seems to be a good representation of the most recent data available in the literature. The oxygen partial pressure for equilibrium between copper and  $Cu_2O$  was obtained from the JANAF tables of thermodynamic data [25].

## 2.6 Parabolic Rate Constant for Copper

The method employed to calculate the parabolic rate constant for the growth of the product copper layer was described in ref. 3; however, some clarification and revision of the derivation is required. The gross rate of advance of the  $Cu/Cu_2O$  interface,  $x$ , is given by Eq. (27) of ref. 3:

$$x = \frac{2v_{Cu} D_{O_2}^{Cu} k_S^{Cu}}{\phi} [P_{O_2}^{1/2} (Cu/Cu_2O) - P_{O_2}^{F 1/2}] = \frac{k_p(Cu)}{\phi} \quad (7)$$

where  $k_p(Cu)$  is the parabolic rate constant\* for the thickening of a layer of copper in the hypothetical case where no copper is left in the aggregate layer behind the reaction front (i.e., where  $\rho = 0$  in Fig. 1);  $k_S^{Cu}$  is the Sieverts' Law constant. The actual rate of thickening of the copper layer when iron oxide rods grow into the copper layer is given by Eq. (28) of ref. 3:

$$\frac{d\phi}{dt} = x - (1 - f) \frac{d\theta}{dt} = \frac{k'_p(Cu)}{\phi} \quad (8)$$

where  $k'_p(Cu)$  is the parabolic rate constant for the thickening of the copper layer when the copper phase grows at the  $Cu/Cu_2O$  interface but it also exists in the aggregate region. The actual rate constant,  $k'_p(Cu)$ , depends on the rates of growth of all of the product phases. The value of  $k_p(Cu)$  in Eq. (7) depends only on the solubility-diffusivity product of copper and on the oxygen potentials at the boundaries of the copper layer. With the insertion of  $x = k_p(Cu)/\phi$  and Eq. (7), into Eq. (8) and use of  $(d\theta/dt) = (\theta/\phi)(d\phi/dt)$ , Eq. (27) in ref. 3, one obtains

$$k'_p(Cu) = k_p(Cu)/[1 + (1 - f)\theta/\phi] \quad (9)$$

\*This constant was denoted  $k'_p$  in ref. 3, unlike the notation used here and in ref. 10.

and

$$\frac{d\phi}{dt} [1 + (1 - f) \frac{\theta}{\phi}] = \frac{k_p^{(Cu)}}{\phi} \quad (10)$$

The value of  $\phi$  can be calculated from Eq. (33) of ref. 3 once the value of  $P_{O_2}^F$  is determined.

### 3. RESULTS AND DISCUSSIONS

The experimental methods that were employed to determine the kinetics of the displacement reaction between iron and  $Cu_2O$  were presented previously [2, 3]. The thickness of the product copper layer,  $\phi$ , the thickness of the copper + oxide product zone,  $\theta$ , and the length of magnetite in the oxide rods,  $\eta$ , were measured for several reaction times at each reaction temperature.

These data were plotted as the square of the thickness or length of a product phase vs. the reaction time. Straight lines were drawn through the data using the method of linear regression. Except for the plots of  $\phi^2$  vs. reaction time at 800 and 850°C, the correlation coefficients from the linear regression were generally greater than 0.95. The straight lines did not all intercept zero product thickness at zero reaction time, which indicates that a single reaction mechanism did not prevail during the entire course of the reaction. The straight lines through the data at later reaction times demonstrate that eventually the displacement reactions were controlled by solid-state diffusion of the reactants through the product phases. The slopes of the straight-line portions of the plots are equal to  $2k'_p$ .

Values of all the kinetic parameters for the Fe/Cu<sub>2</sub>O displacement reaction are presented in Table II. The experimental values of  $k'_p(\text{Fe}_\nu\text{O})$  were calculated from experimental values of  $k_p(\text{oxide})$  and  $k'_p(\text{Fe}_\delta\text{O})$  with the use of Eq. (4). Experimental values of  $(\phi/\theta)$  and  $(n/\xi)$  were calculated using the following equations:

$$\phi/\theta = [k'_p(\text{Cu})/k_p(\text{oxide})]^{1/2} \quad (11)$$

and

$$n/\xi = [k'_p(\text{Fe}_\delta\text{O})/k'_p(\text{Fe}_\nu\text{O})]^{1/2} \quad (12)$$

The volume fraction of oxide in the three-phase product zone was calculated from Eq. (24) of ref. 3; i.e.,

$$f = (1 + \phi/\theta)/(1 + 2V_{\text{Cu}}\bar{V}_{\text{ox}}^{-1}) \quad (13)$$

where  $\bar{V}_{\text{ox}}$  is a weighted average molar volume of the product oxide phase.

The theoretical values of  $P_{\text{O}_2}^F$  that are presented in Table II are greater than  $P_{\text{O}_2}(\text{FeO}/\text{Fe}_3\text{O}_4)$  at each temperature between 800 and 1050°C. Thus, the product oxide rods are expected to comprise wustite and magnetite, which was confirmed experimentally.

The theoretical and experimental values of  $k_p(\text{oxide})$  and  $k'_p(\text{Fe}_\nu\text{O})$  agree well over the entire range of temperature investigated.

Note that  $k'_p(\text{Fe}_v\text{O})$  is approximately equal to  $k_p(\text{oxide})$  because  $n \ll \xi$  (see Table II). Experimental and theoretical values of  $k'_p(\text{Fe}_v\text{O})$  are plotted in Fig. 2. The activation energies obtained from the slopes of the plots of  $\log k'_p(\text{Fe}_v\text{O})$  vs.  $T^{-1}$  are 157,400 and 166,500 J/mole for the experimental and theoretical rate constants, respectively.

Experimental and theoretical rate constants for the growth of the product copper layer agree well within the temperature range of approximately 950-1050°C. Below ~950°C the experimental and theoretical values of  $k'_p(\text{Cu})$  diverge, the divergence increasing as the temperature decreases as illustrated in Fig. 3. The straight line through the data plotted in Fig. 3 was determined by linear regression; the activation energy determined from the slope of the line is 315,300 J/mole. The theoretical activation energy is 240,500 J/mole. The value of  $k'_p(\text{Cu})$  depends both on the rate at which oxygen diffuses through copper and on the rate at which the product oxide rods grow into the product copper layer [see Eq. (8)]. The activation energy from the slope of a plot of  $\log k'_p(\text{Cu})$  vs.  $T^{-1}$  is an activation energy for the net process of growth of the copper layer, and it should not be compared solely to the activation energy for the transport of oxygen in copper as obtained from Eq. (5).

The temperature dependencies of the experimental and theoretical rates of growth of the product oxide rods agree fairly well. Thus, the difference in the temperature dependencies of the experimental and theoretical values of  $k'_p(\text{Cu})$  appears to be related mainly to the dependence on temperature of the flux of oxygen through copper.

Better agreement between experiment and theory is obtained if the absolute magnitudes of the exponential and preexponential terms in the expression for the solubility-diffusivity product for oxygen in copper, Eq. (6), are increased. Using the appropriate limits of precision in Eq. (5) one obtains an activation energy of 255,000 J/mole for the theoretical value of  $k_p'(\text{Cu})$ . The rate constant is increased slightly at 1050°C and decreased slightly at 800°C. The small change in the solubility-diffusivity product has no effect on  $P_{O_2}^F$  or on the other kinetic parameters. In view of the high sensitivity of  $k_p'(\text{Cu})$  to the transport properties of the product phases, the agreement between experimental and theoretical values of  $k_p'(\text{Cu})$  is considered to be good.

The experimental and theoretical values of  $\phi/\theta$  are generally in good agreement. The variations in the experimental and theoretical values of  $\phi/\theta$  with temperature follow approximately the same trends as  $k_p'(\text{Cu})$  and  $k_p'(\text{oxide})$  because of the dependence of  $\phi/\theta$  on these rate constants [Eq. (11)].

The experimental and theoretical values of  $f$ , which were calculated from Eq. (13), are in good agreement at all temperatures in the range of 800 to 1050°C. Note, however, that  $f$  is approximately equal to  $(1 + 2V_{\text{Cu}} V_{\text{Fe}_3\text{O}_4})^{-1}$  when  $\eta \ll \xi$  and  $\phi \ll \theta$ , which is found experimentally. Therefore, the good agreement between experimental and theoretical values of  $f$  simply means that the theory is able to predict  $\eta \ll \xi$  and  $\phi \ll \theta$ .

For temperatures between 950 and 1050°C, the theoretical values of  $k_p'(Fe_{\delta}O)$  are in excellent agreement with the experimental values of  $k_p'(Fe_{\delta}O)$ . The experimental and theoretical values of the rate constant differ sharply for temperatures below 950°C, as shown in Fig. 2. The theoretical values of  $n/\xi$  agree well with the experimental values of  $n/\xi$  for temperatures between 950 and 1050°C, but the two values differ markedly for  $T \gtrsim 950^{\circ}\text{C}$ , as shown in Fig. 4. The variation of  $n/\xi$  with T is simply a reflection of the temperature dependencies of  $k_p'(Fe_{\delta}O)$  and  $k_p'(Fe_{\nu}O)$  because of the dependence of  $n/\xi$  on these rate constants according to Eq. (12).

The theoretical values of  $P_{O_2}^F$  for temperatures above 950°C are less than the oxygen partial pressures at which the mechanism of diffusion in magnetite changes from one involving primarily interstitial cations to one involving primarily vacant cation sites. Thus, the growth of magnetite during a displacement reaction between iron and  $Cu_2O$  above 950°C is supposed to occur by diffusion of iron cations through magnetite by an intersticialcy mechanism.

The use of a correlation factor of unity for an interstitial or intersticialcy mechanism yields theoretical values of  $k_p'(Fe_{\delta}O)$  that are seven to eight times lower than the experimental rate constants at temperatures above 950°C (see Fig. 2). The values of  $P_{O_2}^F$  in the latter case are only a factor or two lower than in the case in which the correlation factor is taken as 0.4. Thus,

the generally good agreement bewteen the other experimental and theoretical kinetic parameters, except  $n/\xi$ , is maintained when the correlation factor is taken as unity.

For temperatures below 950°C, the general mechanism of the displacement reaction between iron and  $Cu_2O$  is qualitatively the same as at higher temperatures; however, the disagreement between theory and experiment for magnetite growth at these lower temperatures indicates that the mechanism for growth must differ. Several reasons could account for the change in the mechanism of growth of magnetite at lower temperatures. For example, a change from predominant lattice diffusion of cations through magnetite at high temperatures to predominant interfacial diffusion of cations at lower temperatures could yield the observed dependence of  $k_p'(Fe_3O_4)$  on temperature. Also, the lower activation energy observed at temperatures below 950°C is characteristic of the activation energy for the growth of magnetite when migration of cations through magnetite by a vacancy mechanism makes a major contribution to the growth process. Values of  $P_{O_2}^F$  that are greater than the oxygen partial pressure for the change from an intersticialcy to a vacancy mechanism of diffusion in magnetite could produce the desired effect. For example, values of  $P_{O_2}^F$  necessary to yield agreement between experimental and theoretical values of  $k_p'(Fe_3O_4)$  at temperatures below 950° are very close to the partial pressures of oxygen for equilibrium between copper and  $Cu_2O$ . The required values of  $P_{O_2}^F$  are, however, greater than the oxygen potentials

necessary to form  $\text{CuFeO}_2$  and they would yield very poor agreement between the experimental and theoretical values of  $k_p'(\text{Cu})$ . It is noted that the morphology of the product zone of the  $\text{Fe}/\text{Cu}_2\text{O}$  displacement reaction at low temperatures does not conform exactly to the model, i.e., at low temperatures the thickness of the product copper layer is not much greater than the spacing between the product oxide rods, as is illustrated in Fig. 5. At low temperatures, the assumption of unidirectional diffusion of oxygen atoms through the product copper layer is apparently not valid. Thus, the kinetic model cannot be applied unambiguously to the  $\text{Fe}/\text{Cu}_2\text{O}$  displacement reaction at low temperatures. Which, if any, of these reasons account for the change in the mechanism of the growth of the magnetite phase cannot be decided at present.

#### 4. CONCLUSIONS

The products of the displacement reaction between iron and  $\text{Cu}_2\text{O}$  for reaction temperatures between 800 and  $1050^\circ\text{C}$  are copper, wustite and magnetite. Excellent agreement is obtained between experimental and theoretical kinetic parameters for reaction temperatures between 950 and  $1050^\circ\text{C}$  if the mechanism of diffusion of iron cations in magnetite for displacement reactions above  $950^\circ\text{C}$  is an interstitialcy mechanism with a correlation factor of 0.4. The mechanism of the growth of magnetite changes at approximately  $950^\circ\text{C}$ . The mechanism of the displacement reaction between Fe and  $\text{Cu}_2\text{O}$  at lower temperatures has not been determined although

interfacial diffusion of cations and enhanced lattice diffusion of cations by a vacancy mechanism in magnetite at lower temperatures may be important factors.

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TABLE I  
QUANTITIES NECESSARY TO CALCULATE THE  
RATE OF GROWTH OF WUSTITE

T°, C	$\bar{v}$	$\bar{V}_{Fe_3O_4}$ , (m <sup>3</sup> /mole) × 10 <sup>5</sup>	$(D_{Fe}^T / g_{Fe})$ , m <sup>2</sup> /s
800	0.9227	1.230	$7.31 \times 10^{-15} P_{O_2}^{-0.118}$
850	0.9194	1.233	$1.28 \times 10^{-13} P_{O_2}^{-0.070}$
900	0.9165	1.236	$1.34 \times 10^{-12} P_{O_2}^{-0.027}$
950	0.9137	1.239	$9.30 \times 10^{-12} P_{O_2}^{0.011}$
1000	0.9111	1.242	$4.55 \times 10^{-11} P_{O_2}^{0.044}$
1050	0.9088	1.245	$1.80 \times 10^{-10} P_{O_2}^{0.076}$

TABLE II. EXPERIMENTAL AND THEORETICAL KINETIC PARAMETERS FOR THE Fe/Cu<sub>2</sub>O DISPLACEMENT REACTION

Parameter	T = 800°C P <sub>O<sub>2</sub></sub> <sup>F</sup> = 1.27 x 10 <sup>-9</sup> N/m <sup>2</sup>	T = 850°C P <sub>O<sub>2</sub></sub> <sup>F</sup> = 1.27 x 10 <sup>-8</sup> N/m <sup>2</sup>	T = 900°C P <sub>O<sub>2</sub></sub> <sup>F</sup> = 1.01 x 10 <sup>-7</sup> N/m <sup>2</sup>	T = 950°C P <sub>O<sub>2</sub></sub> <sup>F</sup> = 4.71 x 10 <sup>-7</sup> N/m <sup>2</sup>	T = 1000°C P <sub>O<sub>2</sub></sub> <sup>F</sup> = 5.70 x 10 <sup>-6</sup> N/m <sup>2</sup>	T = 1050°C P <sub>O<sub>2</sub></sub> <sup>F</sup> = 3.20 x 10 <sup>-5</sup> N/m <sup>2</sup>
Experimental						
k <sub>p</sub> '(oxide), m <sup>2</sup> /s	1.73 x 10 <sup>-12</sup>	1.83 x 10 <sup>-12</sup>	4.47 x 10 <sup>-12</sup>	4.47 x 10 <sup>-11</sup>	8.44 x 10 <sup>-12</sup>	5.05 x 10 <sup>-11</sup>
k <sub>p</sub> '(Fe <sub>2</sub> O <sub>3</sub> ), m <sup>2</sup> /s	1.60 x 10 <sup>-12</sup>	1.79 x 10 <sup>-12</sup>	4.24 x 10 <sup>-12</sup>	4.24 x 10 <sup>-11</sup>	8.07 x 10 <sup>-12</sup>	4.83 x 10 <sup>-11</sup>
k <sub>p</sub> '(Fe <sub>6</sub> O <sub>5</sub> ), m <sup>2</sup> /s	2.78 x 10 <sup>-15</sup>	2.04 x 10 <sup>-16</sup>	3.04 x 10 <sup>-15</sup>	6.16 x 10 <sup>-16</sup>	4.23 x 10 <sup>-15</sup>	4.51 x 10 <sup>-15</sup>
k <sub>p</sub> '(Cu), m <sup>2</sup> /s	1.27 x 10 <sup>-16</sup>	3.79 x 10 <sup>-16</sup>	3.08 x 10 <sup>-16</sup>	1.26 x 10 <sup>-15</sup>	2.54 x 10 <sup>-15</sup>	8.84 x 10 <sup>-15</sup>
(φ/θ)	8.56 x 10 <sup>-3</sup>	1.44 x 10 <sup>-2</sup>	8.3 x 10 <sup>-3</sup>	1.74 x 10 <sup>-2</sup>	1.73 x 10 <sup>-2</sup>	2.45 x 10 <sup>-2</sup>
(n/ξ)	4.2 x 10 <sup>-2</sup>	1.06 x 10 <sup>-2</sup>	2.68 x 10 <sup>-2</sup>	1.23 x 10 <sup>-2</sup>	4.72 x 10 <sup>-1</sup>	4.76 x 10 <sup>-1</sup>
f	4.67 x 10 <sup>-1</sup>	4.69 x 10 <sup>-1</sup>	4.67 x 10 <sup>-1</sup>	4.71 x 10 <sup>-1</sup>	4.80 x 10 <sup>-1</sup>	4.83 x 10 <sup>-1</sup>
Theoretical						
k <sub>p</sub> '(oxide), m <sup>2</sup> /s	4.18 x 10 <sup>-12</sup>	4.18 x 10 <sup>-12</sup>	4.18 x 10 <sup>-11</sup>	4.18 x 10 <sup>-11</sup>	8.53 x 10 <sup>-12</sup>	1.72 x 10 <sup>-11</sup>
k <sub>p</sub> '(Fe <sub>2</sub> O <sub>3</sub> ), m <sup>2</sup> /s	4.08 x 10 <sup>-12</sup>	4.08 x 10 <sup>-12</sup>	4.08 x 10 <sup>-11</sup>	4.08 x 10 <sup>-11</sup>	1.70 x 10 <sup>-15</sup>	4.17 x 10 <sup>-15</sup>
k <sub>p</sub> '(Fe <sub>6</sub> O <sub>5</sub> ), m <sup>2</sup> /s	6.16 x 10 <sup>-16</sup>	6.16 x 10 <sup>-16</sup>	6.16 x 10 <sup>-15</sup>	6.16 x 10 <sup>-15</sup>	3.86 x 10 <sup>-15</sup>	1.05 x 10 <sup>-14</sup>
k <sub>p</sub> '(Cu), m <sup>2</sup> /s	1.26 x 10 <sup>-15</sup>	1.26 x 10 <sup>-15</sup>	1.26 x 10 <sup>-14</sup>	1.26 x 10 <sup>-14</sup>	2.10 x 10 <sup>-2</sup>	2.44 x 10 <sup>-2</sup>
(φ/θ)	1.74 x 10 <sup>-2</sup>	1.41 x 10 <sup>-2</sup>	1.56 x 10 <sup>-2</sup>			
(n/ξ)	1.23 x 10 <sup>-2</sup>	4.74 x 10 <sup>-1</sup>	4.76 x 10 <sup>-1</sup>			
f	4.71 x 10 <sup>-1</sup>	4.80 x 10 <sup>-1</sup>	4.83 x 10 <sup>-1</sup>			

LIST OF FIGURES

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- FIGURE 3. The dependence on reaction temperature of the experimental and theoretical parabolic rate constants for the growth of the product copper layer.
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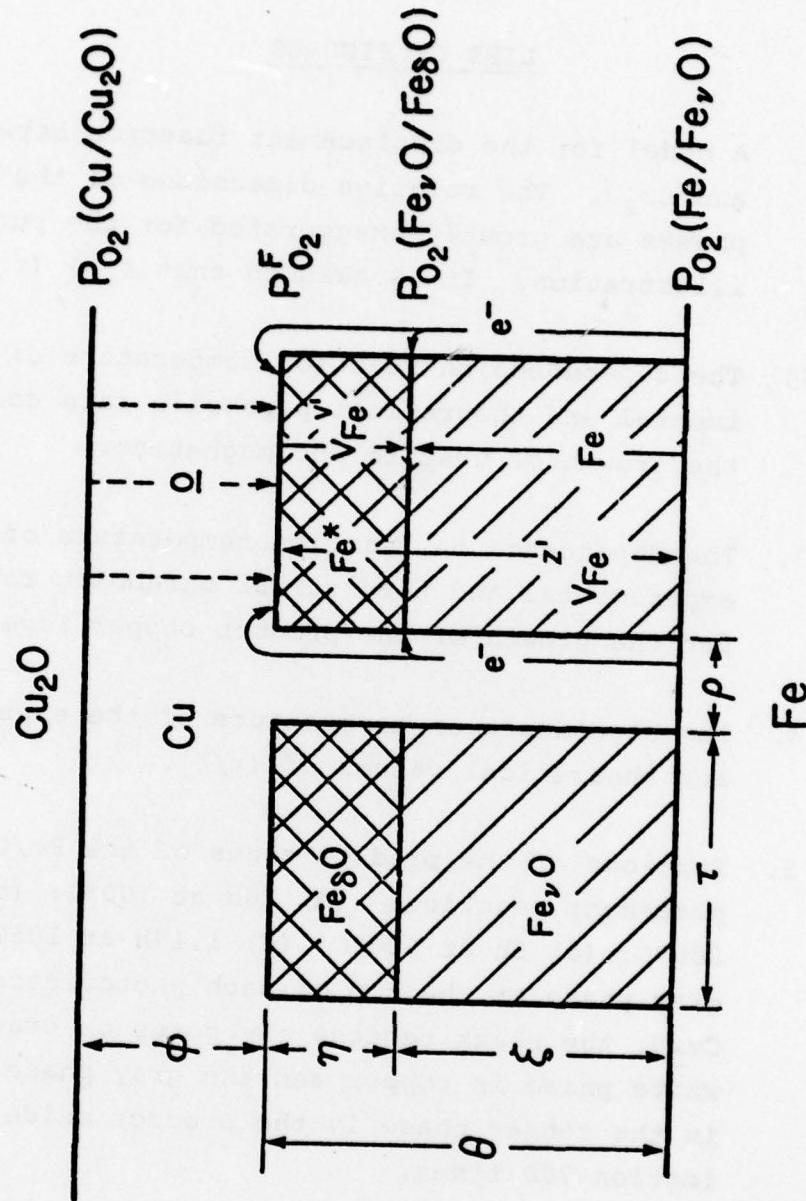


FIGURE 1. A model for the displacement reaction between iron and  $\text{Cu}_2\text{O}$ . The relative dimensions of the product phases are greatly exaggerated for the purpose of illustration. It is assumed that  $\phi > (\tau + \rho)$ .

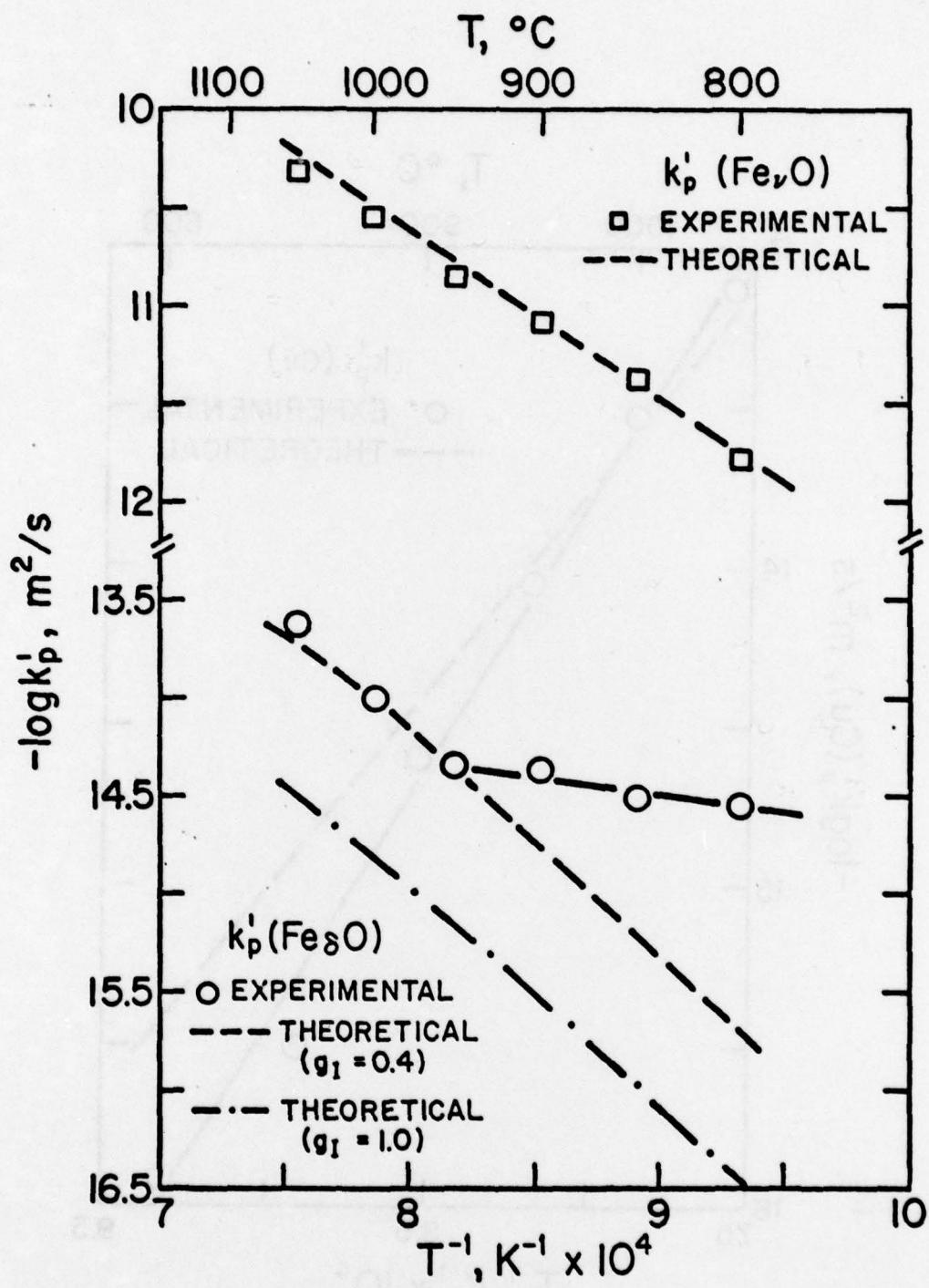


FIGURE 2. The dependence on reaction temperature of the experimental and theoretical parabolic rate constants for the growth of wustite and magnetite.

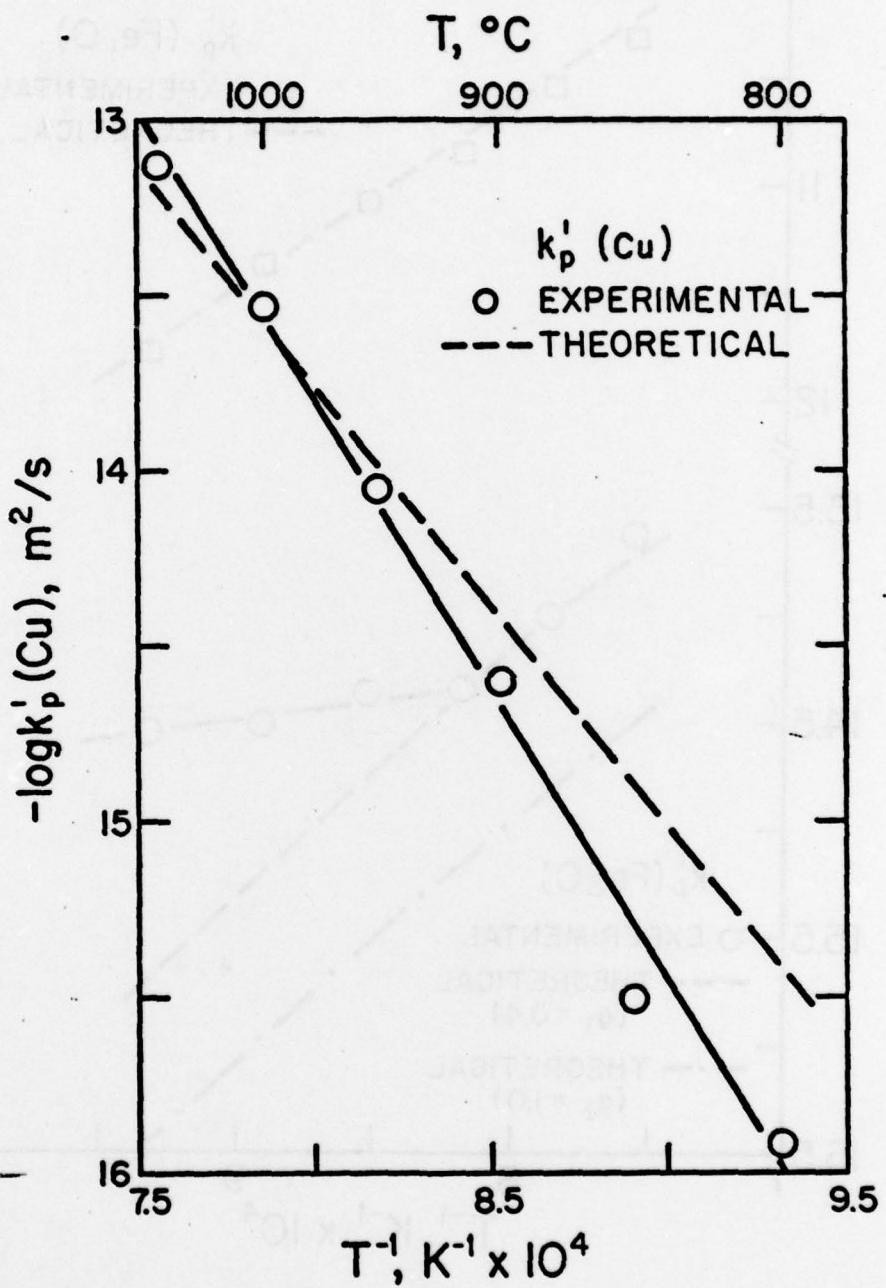


FIGURE 3. The dependence on reaction temperature of the experimental and theoretical parabolic rate constants for the growth of the product copper layer.

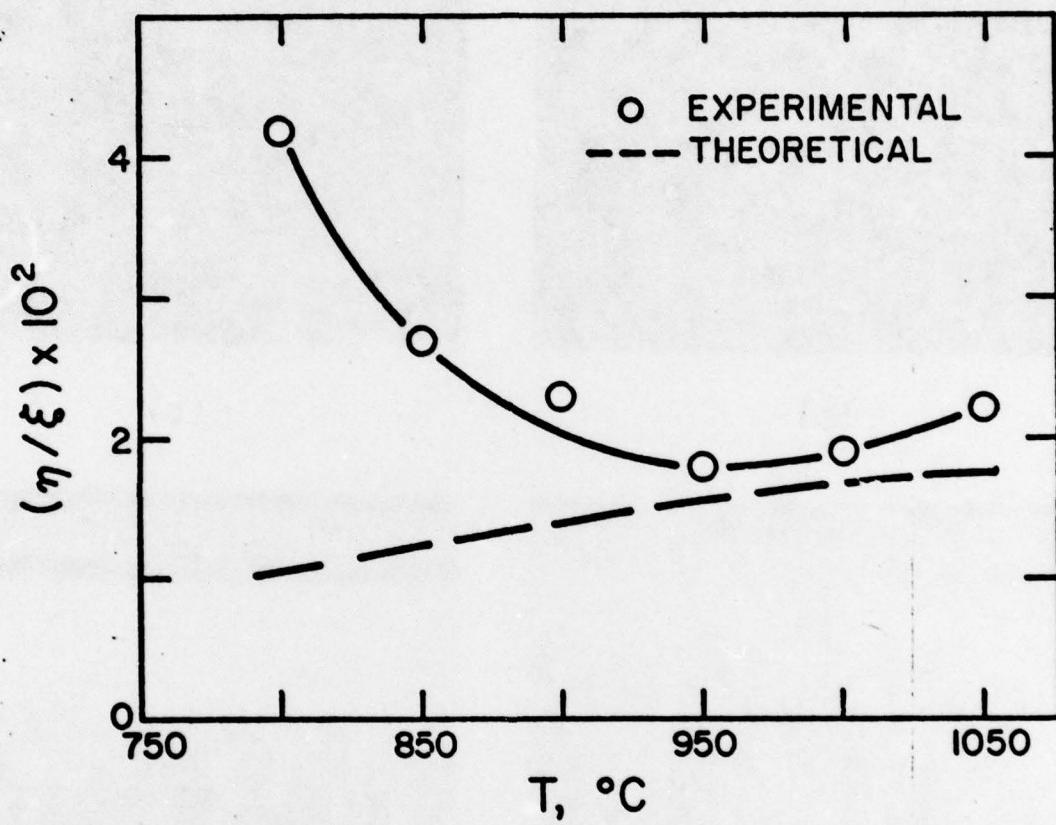


FIGURE 4. The dependence on temperature of the experimental and theoretical values of  $(\eta/\epsilon)$ .



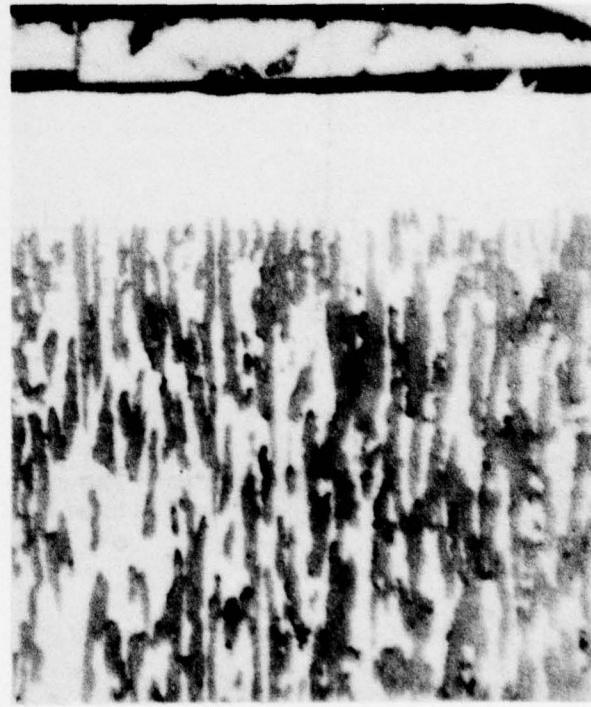
(a)



(b)



(c)



(d)

Figure 5